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Selective extraction of strontium with supercritical fluid carbon dioxide

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Abstract

Strontium (Sr^{2+}) can be selectively extracted from aqueous solutions into supercritical fluid CO_2 at 60 °C and 100 atm with dicyclohexano-18-crown-6 (DC18C6) using $\text{CF}_3(\text{CF}_2)_6\text{CO}_2^-$ (PFOA⁻) or $\text{CF}_3(\text{CF}_2)_6\text{CF}_2\text{SO}_3^-$ (PFOSA⁻) as a counter anion; at a mole ratio of Sr^{2+} : DC18C6 : PFOA⁻ = 1:10:50, the extraction of Sr (5.6×10^{-5} M) from water at pH 3 is near quantitative whereas Ca^{2+} and Mg^{2+} at equal concentration are only extracted to a level of 7 and 1%, respectively; PFOSA⁻ is an effective counter anion for selective extraction of Sr^{2+} from 1.3 M HNO_3 with DC18C6 in supercritical CO_2 .

Research in selective transport of metal ions in supercritical (sc)- CO_2 is of considerable current interest because of its potential applications in a variety of chemical processes which may be carried out in this environmentally friendly solvent.^{1,2} Selective extraction of alkali metal and alkaline earth metal ions from aqueous solutions to organic solvents with crown ethers is well established in the literature. Extraction of these hard metal ions with crown ethers in scCO_2 is expected to be difficult because of limited solubilities of the resulting metal complexes in CO_2 .³ It is known that fluorinated metal chelates are CO_2 -philic.⁴ Thus, fluorination of ligands is one method of increasing solubility of metal complexes in CO_2 . This approach requires the design and synthesis of specific fluorinated macrocyclic compounds. Another method is to extract crown ether-metal complexes as ion-pairs into scCO_2 utilizing fluorinated counteranions. We report for the first time the successful extraction of Sr^{2+} from aqueous media into scCO_2 utilizing a macrocyclic compound and a fluorinated counter anion.

It is known that 18-membered crown ethers with cavity diameters in the range 2.6–2.8 Å are the most suitable hosts for Sr^{2+} (2.2 Å).⁵ For example, ^{90}Sr can be selectively extracted from nitric acid solutions with dicyclohexano-18-crown-6 (DC18C6) dissolved in a paraffinic or halogenated solvent, where nitrate serves as the counter anion.⁶ This macrocyclic system is currently being evaluated for removing ^{90}Sr ($t_{1/2} = 30$ years), a major uranium fission product, from the high level acidic nuclear wastes stored at the Idaho DOE site. However, disposal of organic liquid wastes generated from any solvent extraction process is a problem of environmental concern today because of changing government regulations. Supercritical fluid extraction provides several advantages over conventional solvent extraction including minimization of waste generation, allowing rapid separation of

extracted metal complexes, and enhancement of transport speed due to high diffusivity of the supercritical fluid.

The high-pressure apparatus for supercritical fluid extraction of aqueous systems has been described previously.⁷ A measured amount of DC18C6 and a fluorinated counter anion, both dissolved in chloroform, was loaded into a 10 mL stainless steel extraction vessel and evaporated to dryness on a water bath at 60 °C with flowing nitrogen gas. 5 mL of an aqueous solution containing a mixture of Sr^{2+} , Ca^{2+} and Mg^{2+} at 5.6×10^{-5} M each were then added to the vessel. The vessel was pressurized with CO_2 and heated to the desired temperature. After 20 min of static extraction, the exit valve was opened and the system was flushed with scCO_2 for 20 min. The aqueous solution before and after extraction was analyzed by an ICP/AES instrument for metal contents.

DC18C6 is quite soluble in scCO_2 , with a solubility estimated to be $> 10^{-2}$ mol L^{-1} at 60 °C and 100 atm, according to our experiments. Direct extraction of Sr^{2+} (5.6×10^{-5} M) with an excess of DC18C6 (5.4×10^{-4} M) in supercritical CO_2 showed virtually no detectable extraction of Sr^{2+} from water (Table 1) or from a 1.3 M nitric acid solution (Table 2). With the addition of a fluorinated carboxylic acid such as pentadecafluoro-*n*-octanoic acid (HPFOA), extraction of Sr^{2+} from water with DC18C6 in scCO_2 became significant. The pH of water in equilibrium with scCO_2 under the experimental conditions should be *ca.* 2.9 according to a previous study.⁸ Because of the inductive effect of the fluorinated group in HPFOA, the pK_a value of this perfluorinated acid is *ca.* 1. Therefore, HPFOA is expected to exist as the anionic form PFOA^- under the specified experimental conditions of this water/ scCO_2 system. With a concentration of $\text{Sr}^{2+} = 5.6 \times 10^{-5}$ M and a mol ratio of Sr^{2+} : DC18C6: $\text{PFOA}^- = 1:5:10$, *ca.* 36% of the Sr^{2+} was removed from the water after 20 min of static extraction followed by 20 min of dynamic flushing at 60 °C and 100 atm. The percentage extraction of Ca^{2+} and Mg^{2+} (at equal concentration as Sr^{2+}) under the same conditions was negligible (3% or less). By doubling the concentration of DC18C6 (*i.e.* at a mol ratio of Sr^{2+} : DC18C6: $\text{PFOA}^- = 1:10:10$), *ca.* 52% of the Sr^{2+} in the water phase was removed at 60 °C and 100 atm. Assuming the percentage Sr extraction from water represents equilibrium partition, we may estimate the distribution coefficient D_{Sr} (concentration of Sr in the CO_2 phase over that in the aqueous phase) from the extraction data using the relationship $D_{\text{Sr}} = (C_i - C_f)/C_f$, where C_i and C_f are the concentration of Sr in water before and after the extraction, respectively. The D_{Sr} value appears to double (from 0.56 to 1.08) when the Sr^{2+} : DC18C6: PFOA^- ratio is increased from 1:5:10 to 1:10:10, suggesting the stoichiometry of Sr to DC18C6 in the complex is most likely 1:1. In the absence of DC18C6, extraction of Sr^{2+} was negligible at 60 °C and 100 atm (Sr^{2+} : $\text{PFOA}^- = 1:10$). Pressure has a minor effect on Sr^{2+} extraction. At 60 °C and 300 atm, the percentage extraction of Sr^{2+} was increased to 58% at a mol ratio of Sr^{2+} : DC18C6: $\text{PFOA}^- = 1:10:10$.

The extraction of Sr^{2+} showed a strong dependence on PFOA^- concentration. With a mol ratio of Sr^{2+} : DC18C6: $\text{PFOA}^- = 1:10:50$, nearly quantitative extraction (98%) of Sr^{2+} from water into scCO_2 was observed at 60 °C and 100 atm. Under these conditions, Ca^{2+} and Mg^{2+} were extracted at 7 and 1%, respectively. Selective transport of Sr^{2+} in the presence of Ca^{2+} and Mg^{2+} from an aqueous solution to the scCO_2 phase apparently can be achieved using DC18C6 and PFOA^- according to the results shown in Table 1. Based on the extraction data, we also estimated the variation of D_{Sr} with respect to the HPFOA concentration. Values of D_{Sr} increase from 1.1 to *ca.* 49 when the concentration of the HPFOA is increased by a factor of five. This suggests that the Sr^{2+} -crown complex extracted into the supercritical fluid probably involves 2 PFOA^- . Accurate measurement of D values in supercritical fluids requires a different experimental design. The preliminary results obtained from this supercritical fluid extraction study appear consistent with the charge neutralization requirement and the general concept of crown ether extraction.

The rate of extraction of Sr^{2+} from aqueous phase into scCO_2 with DC18C6 and HPFOA is reasonably fast. At 60 °C, 100 atm and with a Sr^{2+} : DC18C6:PFOA⁻ ratio of 1:10:10 in water, the supercritical fluid extraction of Sr was found to be 11, 49, 52 and 51, for 5, 11, 19 and 30 min of static extraction, respectively. The dynamic flushing time for these experiments was fixed at 20 min. Under the specified experimental conditions, 20 min of static extraction appear sufficient to reach equilibrium.

When perfluoro-1-octanesulfonic acid tetraethylammonium salt, NEt_4 PFOSA, was used instead of HPFOA, the extraction efficiency for Sr^{2+} from water became higher but the selectivity for Sr^{2+} over Ca^{2+} and Mg^{2+} was reduced. At a Sr^{2+} : DC18C6: NEt_4 PFOSA ratio of 1:10:10, the percentage extraction of Sr^{2+} , Ca^{2+} and Mg^{2+} were 99, 66, and 2%, respectively. If the potassium salt KPFOSA was used in the extraction instead of the NEt_4^+ salt, selective extraction of Sr^{2+} was observed. For KPFOSA, the extraction of Sr^{2+} , Ca^{2+} and Mg^{2+} were 97, 8 and 2%, respectively (Table 1). The cause of the unusual Ca^{2+} extraction from water with NEt_4 PFOSA and DC18C6 in supercritical CO_2 is not known.

Selective extraction of Sr^{2+} by scCO_2 with DC18C6 and a fluorinated counter anion was also observed in 1.3 M HNO_3 (Table 2). The extraction of Sr^{2+} in the acid solution with a Sr^{2+} :DC18C6:KPFOSA ratio of 1:10:50 was 60% whereas Ca^{2+} and Mg^{2+} were extracted at a level of *ca.* 8 and 2%, respectively. The extraction efficiency of Sr^{2+} increased to 76% when the crown ether concentration was doubled (Table 2). NEt_4 PFOSA did not show unusual Ca^{2+} extraction from the acid solution when it was used with DC18C6 in scCO_2 . The fluorinated carboxylic acid HPFOA is less effective than the fluorinated sulfonic acid for Sr^{2+} extraction in the acid solution. In general, a high selectivity of extracting Sr^{2+} over Ca^{2+} and Mg^{2+} was observed in all the acid solution experiments. It should be pointed out that the high level acidic nuclear wastes stored at the Idaho DOE site is in 1.3 M HNO_3 .

The experimental results obtained from this study suggest that Sr^{2+} in water or in 1.3 M nitric acid can be selectively extracted as ion-pairs with DC18C6 and a fluorinated counter anion in supercritical fluid CO_2 . Utilizing the same principle of synergism, other alkali metal and alkaline earth metal ions probably can also be extracted in supercritical CO_2 with proper selection of macrocyclic hosts and perfluorinated counter anions. The possibility of extracting and transporting alkali metals and alkaline earth metals selectively in supercritical CO_2 suggests a number of potential applications including removal of major fission products ^{137}Cs and ^{90}Sr from aqueous or acidic nuclear wastes and phase transfer catalysis for specific reactions in supercritical CO_2 .

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Table 1

Extraction of Sr^{2+} , Ca^{2+} and Mg^{2+} from water by sc fluid CO_2 containing DC18C6 and perfluorinated counter anion PFOA^- or PFOSA^- at 60 °C and 100 atm^a

Mol ratio	Extraction (%)			
	Sr^{2+} :DC18C6:HPFOA	Sr^{2+}	Ca^{2+}	Mg^{2+}
1 10	0	1	0	0
1 0	10	4 ± 1	1 ± 1	1 ± 1
1 5	10	36 ± 2	1 ± 1	1 ± 1
1 10	10	52 ± 2	2 ± 1	1 ± 1
1 10	50	98 ± 2	7 ± 2	2 ± 1
NEt ₄ PFOSA				
1 0	10	12 ± 2	6 ± 2	2 ± 1
1 5	10	98 ± 2	45 ± 4	2 ± 1
1 10	10	99 ± 1	66 ± 5	2 ± 1
KPFOSA				
1 10	10	97 ± 2	8 ± 2	2 ± 1

^aThe aqueous solution contained a mixture of Sr^{2+} , Ca^{2+} and Mg^{2+} with a concentration of 5.6×10^{-5} M each; pH of water under equilibrium with $\text{scCO}_2 = 2.9$; 20 min static followed by 20 min dynamic flushing at a flow rate of 2 mL min⁻¹. HPFOA = $\text{CF}_3(\text{CF}_2)_6\text{CO}_2\text{H}$; NEt₄PFOSA = $\text{NEt}_4[\text{CF}_3(\text{CF}_2)_6\text{CF}_2\text{SO}_3]$; KPFOSA = $\text{CF}_3(\text{CF}_2)_6\text{CF}_2\text{SO}_3\text{K}$.

Table 2

Extraction of Sr^{2+} , Ca^{2+} and Mg^{2+} from 1.3 M HNO_3 by scCO_2 containing DC18C6 and HPFOA or PFOSA salt at 35 °C and 200 atm^a

Mol ratio	Extraction (%)			
	Sr^{2+} :DC18C6:HPFOA	Sr^{2+}	Ca^{2+}	Mg^{2+}
1 10	0	1	0	0
1 10	50	18 ± 2	2 ± 1	1 ± 1
KPFOSA				
1 10	50	60 ± 3	8 ± 2	2 ± 1
1 20	50	76 ± 3	8 ± 2	1 ± 1
NEt_4PFOSA				
1 10	50	61 ± 3	7 ± 2	2 ± 1

^aThe acid solution contained a mixture of Sr^{2+} , Ca^{2+} and Mg^{2+} with a concentration of 5.6×10^{-5} M each; 20 min static followed by 20 min dynamic flushing at a flow rate of 2 mL min⁻¹.